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Structure-Sensitive Catalytic Oxidation of Butenes on Molybdenum Trioxide Crystallites

We have shown previously that the oxidations of 1-butene and isobutene on graphite-supported α-MoO_3 "small" crystallites ($\approx$10 μm) are structure-sensitive catalytic reactions (*1*). We considered it important to extend the work to studies on larger crystals and to different methods of preparation. We now demonstrate that there is a similar effect for 1-butene and 2-butene oxidation catalyzed by "large" ($\approx$1 mm) unsupported α-MoO_3 crystallites. In view of the widely different crystal magnitudes and modes of preparation for the two series of catalysts, the coincidence of catalytic properties indicates the absence of spurious factors (impurities, size or support effects).

The preparation of α-MoO_3 needle-like crystals by sublimation at 800°C in an oxygen current was described before (*2*). A large batch of sublimed trioxide was separated by sieving into seven fractions. A statistical measurement of average dimensions performed for each fraction (Zeiss particle-size Analyzer TGA10) was used to calculate the relative extents of the three principal exposed crystal planes; the crystal shape, shown in Fig. 1 of Ref. (*2*), is essentially a parallelepiped with a large "basal" face (010), a thin "side" face (100), and a small, sometimes ill-defined, "apical," face (001) + (101). The indexing of the orthorhombic α-MoO_3 structure described by Kihlborg (*5*) is used. From the length (L), width (l), and thickness (e) the percentage of different faces exposed and the total surface area of each sample were calculated (Table 1).

Catalytic tests were run in a continuous-flow isothermal reactor with chromatographic analysis of in- and outgoing gas streams, at 400°C/1 atm.

The reactant mixture was butene, oxygen, and helium at molar ratio $C_4H_8/O_2/He = 10/20/70$. This was fed at a constant rate (3–5 liters/h) such that butene conversion was about 3%. Due to the low surface area and activity of the catalyst, a large sample (up to 15 g) of undiluted α-MoO_3 was charged into the reactor, and dead spaces were carefully avoided. Steady-state conditions were obtained after 1 h on stream; during this first period, a slight decrease of activity but no change of selectivity was noted. Under these "initial" conditions, 1- and 2-butene gave qualitatively identical mixtures of products, namely, the three butenes (1-butene, *cis*-2-butene and *trans*-2-butene), butadiene, carbon monoxide, and carbon dioxide.

Selectivities were calculated on the basis of either the butene in the feed (1- or 2-butene) or the total butenes (1 + 2). In this last case, double-bond isomers were counted as a unique reagent.

We present the experimental results for 1-butene and 2-butene separately.

1-Butene. Catalytic runs on the seven samples of Table 1 are summarized in terms of selectivity (%), in Table 2. The most striking feature is the regular increase of the butadiene/carbon oxide ratio when the α-MoO_3 crystallite size decreases. At the same time, the butadiene selectivities on total butenes increase from 50 to 80%.

The double-bond migration accounts for one-third to two-thirds of the reacted 1-butene but no correlation is found with the oxidation path; this point was confirmed by

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TABLE 1

Average Dimensions and Percentages of Exposed Faces of α-MoO_3 Crystallites

Sample code	$\bar{L}_{mm}$	$\bar{l}_{mm}$	$\bar{e}_{mm}$	% (010)	% (100)	% (001)	Surface area (cm^2/g)
S_5	4.01	0.79	0.08	89.2	9.0	1.8	59
S_4	2.60	0.473	0.062	86.6	11.4	2.0	79
S_3	1.930	0.329	0.058	82.9	14.6	2.5	89
S_2	1.511	0.159	0.040	78.2	19.7	2.1	136
S_1	0.859	0.112	0.029	77.4	20.0	2.6	189
S_{-1}	0.292	0.027	0.008	75.5	22.4	2.1	705
S_{-2}	0.132	0.013	0.005	70.3	27	2.7	1211

determinations of activation energies (*3*). *cis*/*trans* ratios are above the equilibrium value of 0.7; this feature is also found in 1-butene isomerization on alumina (*4*).

The treatment of the oxidation data in order to define the structure sensitivity more precisely was detailed in other papers (*1*, *2*). When the ratio of butadiene/carbon oxide selectivity is plotted against the ratio of side and basal faces, the points corresponding to six of the catalyst samples (out of seven) fall on a straight line (Fig. 1). The slope is close to 12 and the intercept close to zero. We may conclude that:

—butadiene is formed on the (100) side face of crystallites,

—carbon oxides are formed on the (010) basal face,

—the side face (100) is 12 times more active than the basal face (010) (intrinsic rates),

—the apical face action is negligible, because of its low intrinsic activity, its low area, or both.

trans-2-Butene. Results of catalytic runs on six of the α-MoO_3 samples of Table 1 are reported in Table 3.

A regular increase of butadiene selectivity (on total butene) with decreasing crystal size is again observed (60–80%) and is clearly shown if the butadiene/carbon oxide ratio is calculated. The formation of double-bond isomers (1-butene and *cis*-2-butene) is comparatively slow in the present case: 30 to 44% of the converted *trans*-2-butene (against 35 to 66% in the case of 1-butene).

Interestingly, the oxidation rates are identical for the 1- and 2-butenes as shown when considering the most active catalysts (S_{-1} and S_{-2}); the isomerization rates and consequently the total rates are lower for *trans*-2-butene. The plot of the butadiene/carbon oxide ratio against the ratio of side and basal crystal faces is again a straight

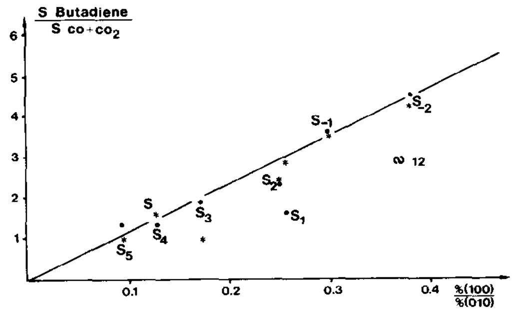

FIG. 1. Ratio of butadiene and carbon oxide selectivity vs ratio of side and basal faces of α-MoO_3 catalysts (sample code indicated in Table 1) in the oxidation of 1-butene (∗) and *trans*-2-butene (●) at 400°C.

TABLE 2

Initial Selectivities for 1-Butene Catalysis on Different Samples of α-MoO_3 Microcrystals at 400°C

Sample code		Product selectivity (%)		Butadiene/carbon oxides
		On 1-butene	On butenes	
S_5	2-Butenes	47.9	—	1
	Butadiene	25.7	49.3	
	Carbon oxides	26.4	50.7	
S_4	2-Butenes	51.5	—	1.6
	Butadiene	29.9	61.7	
	Carbon oxides	18.6	38.3	
S_3	2-Butenes	38.2	—	1
	Butadiene	30.7	49.8	
	Carbon oxides	31.1	50.2	
S_2	2-Butenes	34.9	—	2.4
	Butadiene	45.9	70.5	
	Carbon oxides	19.2	29.5	
S_1	2-Butenes	38.8	—	
	Butadiene	45.8	74.8	2.97
	Carbon oxides	15.4	25.2	
S_{-1}	2-Butenes	65.6	—	3.60
	Butadiene	27	78.4	
	Carbon oxides	7.4	21.6	
S_{-2}	2-Butenes	65.6	—	4.37
	Butadiene	28	81.4	
	Carbon oxides	6.4	18.6	

TABLE 3

Initial Selectivities for *trans*-2-Butene Catalysis on Different Samples of α-MoO_3 Microcrystals at 400°C

Sample code		Product selectivity (%)		Butadiene/carbon oxides
		On 2-butene	On butenes	
S_4	1-Butene	9.7	—	1.4
	cis-2-Butene	19.1	—	
	Butadiene	41.5	58.3	
	Carbon oxides	29.7	41.7	
S_3	1-Butene	9.9	—	2
	cis-2-Butene	20.5	—	
	Butadiene	46	66.1	
	Carbon oxides	23.6	33.9	
S_2	1-Butene	7.9	—	
	cis-2-Butene	30.1	—	2.3
	Butadiene	43	69.3	
	Carbon oxides	19	30.7	
S_1	1-Butene	9	—	
	cis-2-Butene	19.4	—	1.6
	Butadiene	44.2	61.7	
	Carbon oxides	27.4	38.3	
S_{-1}	1-Butene	14.3	—	
	cis-2-Butene	31.6	—	3.8
	Butadiene	42.8	79.1	
	Carbon oxides	11.3	20.9	
S_{-2}	1-Butene	13.7	—	
	cis-2-Butene	30.1	—	4.6
	Butadiene	46.2	72.3	
	Carbon oxides	9.9	17.7	

line with a slope of 12 and an intercept close to zero, practically identical to the plot for 1-butene (Fig. 1).

We may conclude that:

—1-butene and 2-butene oxidation reactions on α-MoO_3 crystallites have identical rates and selectivities,

—double-bond isomerization rates are different for 1- and 2-butene,

—the two types of reactions are not correlated,

—butadiene formation is mostly catalyzed by the (100) side face and carbon oxide formation by the (010) basal face; the rate ratio (intrinsic) for these two processes is close to 12 at 400°C.

As a consequence, the higher butadiene selectivity (80%) is linked to the α-MoO_3 crystallites with a higher percentage of side face (100).

In the present work, these correspond to the smaller crystallites (sample S_{-2}); we have shown elsewhere (*3*) that a representative commercial sample of α-MoO_3 (Merck; 1.5 m^2/g) exhibits the same butadiene selectivity (80%). Conventional preparations of α-MoO_3 must produce crystallites similar in shape to the finer sublimed crystallites.

Due to the poor precision on estimated total surface area (Table 1) a direct calculation of the butadiene intrinsic activity of face (100) leads to rather scattered results, but an indicative average value (for all samples and both butenes) is 3.8 mmol/h · m^2.

Relative intrinsic activities of the different crystal faces are summarized in the following matrix:

Product	Face		
	Basal (010)	Side (100)	Apical (001)
Butadiene	0	12	—
Carbon oxides	1	0	—
Total	1	12	—

Let us now briefly discuss the data and draw conclusions.

The above results must be compared with data for graphite-supported molybdenum trioxide catalysts (*1*) in which α-MoO_3 crystallites are much smaller (≈10 μm). The same crystal form is observed, but apical facets [mostly (101)] are more developed (up to 18% of total surface); these account for less than 3% of the total surface for sublimed α-MoO_3 needles (Table 1). In consequence, the specific activity of supported catalysts is distinctly higher (due to their large surface area) and the catalytic effect of the apical face is no longer negligible.

The results for 1-butene conversion are summarized by the following matrix of relative intrinsic activities at 400°C:

Product	Face		
	Basal (010)	Side (100)	Apical (101)
Butadiene	2.4	9.6	1.1
Carbon oxides	1	0	0.2
Total	3.4	9.6	1.3

—Butadiene is produced on all crystal faces, but mainly and most selectively on the side (100) face.

—Carbon oxides are mostly produced on the basal (010) face, with a slight activity of the apical (101) face.

—The side face activity for butadiene is about 10 times as large as the basal face activity for carbon oxides.

This pattern is consistent with the findings on unsupported "large" crystallites of α-MoO_3 if the differences in sizes (overall activity) and shapes (apical faces) are taken into account. In particular, the ratios of butadiene activity of (100) to carbon oxide activity of (010) are, for the three cases at hand, in the range 9–12, and the side face is specific for butadiene formation.

The overall intrinsic activities of crystallite faces, viz.

$$(100) > (010) > (101) \text{ or } (001)$$

combined with their relative surfaces, viz.,

$$(010) > (100) > (101) \text{ or } (001)$$

indicate that most of the catalytic oxidation activity is localized at the side and basal crystal faces; the least active and developed apical face plays a minor role.

In this respect the "large" α-MoO_3 needles behave as "two-face" crystallites and present an abridged pattern of activities when compared to supported α-MoO_3 crystallites.

In conclusion, the good agreement between results obtained from two series of α-MoO_3 catalysts covering a 100-fold change in crystal size and two different precursors of the active phase and methods of preparation proves that the structure sensitivity in catalysis is not a crystal size or impurity effect. This remark which was shown to be valid for catalytic oxidation of alcohols (*2*, *6*) is here extended to olefins.

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